THE USE OF SHORT HALF-LIFE RADIOISOTOPES IN TAGGING COAL

Robert F. Stewart

U. S. Department of the Interior, Morgantown Coal Research Center
Bureau of Mines, Morgantown, W. Va.

An important use of radioisotopes in research on coal processing and coal research is in tagging the coal to determine the path it takes through the process under investigation. The application of radioactive tagging, however, is often limited by radiation hazards, process contamination, or the expense of radiation facilities. Although only a small amount of radioactive material is initially required to tag the material, equipment may soon become contaminated, decreasing the sensitivity of measurement and requiring successively larger amounts of radioactivity for subsequent tests. In addition, the product is often contaminated and there is the problem of disposal of radioactive materials. From a practical viewpoint a method is needed which is simple, accurate, completely safe and economical.

The use of short-lived radioisotopes having a half-life of perhaps one hour would solve these difficulties. However, this also introduces the problem of supplying such an isotope in useable form. The use of gamma "cows" or "milkers" solves this problem.

Method of Tagging Coal with a Short-Lived Radioisotope. One of the great advantages of radioactive tracers in industrial applications is the use of tracers with half-lives of one hour or less. This means that a few hours after they are used the radioactivity has completely disappeared. Such a tracer can be used without contaminating equipment or leaving any residual radioactivity. Since the radioactivity of short-lived tracers dies out in less than a day, however, one problem with them is a source of supply. This has been solved by the use of gamma "cows" or "milkers," including a means of separating the parent-daughter isotopes. In this method, a longer-lived parent element is stored for future use, then, when needed, the short half-life daughter element is separated or milked from the parent and used to tag the process material.

An example of a gamma cow is the element germanium-68 which is available in millicurie amounts as germanium chloride dissolved in about 20 ml. of dilute acid. The continuously produced daughter-isotope gallium-68 can be extracted as gallium chloride from the parent and used immediately. Germanium-68, the parent radioisotope, has a half-life of 250 days and can be used as a source of gallium-68 for several years before the activity of the germanium-68 becomes too low for use. During these years, the germanium can be extracted for gallium every ten minutes or as needed.

The extraction or milking procedure is very simple. Twenty milliliters of 25 percent acetylacetone are added to the germanium solution in a separatory funnel, shaken vigorously and allowed to clarify. Most of the acetylacetone solution, which contains only the daughter gallium, is decanted or withdrawn with an automatic pipette, leaving all of the germanium solution for subsequent extractions. The gallium solution can now be added to powdered coal, dried, and the tagged coal used immediately. The gallium solution can be injected directly into a pipeline, or if miscibility with water is required, the gallium may be extracted with an aqueous solution. Gallium-68, with a half-life of about one hour, emits both beta and gamma radiation. Its gamma radiation has an energy of 1.1 Mev, which means it can be effectively measured through an iron pipe or at a distance of several feet.

Nearly 1 millicurie of gallium can be obtained by each extraction from a stock of 2 millicuries of germanium. This provides enough radioactivity for most tracer applications. Regardless of how the short-lived gallium is used, it naturally disintegrates in a few hours forming stable zinc-68.

Use of Coal Tagged with Gallium-68. Gallium-68 is particularly useful in short-duration measurements of flow paths, flow rates, mixing operations, etc., which are completed in a few hours, and where contamination of product or equipment must be avoided. The tagged material can be added to a process stream with complete assurance that all radioactivity will be gone the next day.

Coal particles have been tagged with gallium-68 to measure reaction time of the coal and steam in a laboratory-scale coal gasifier. This gasifier is based on the falling particle technique (1) and is used to determine the reaction rate of pulverized coal as it drops through a steam atmosphere inside a 3-inch-diameter, 9-foot long tube at temperatures from 1,800 to 2,400° F. One of the problems with this apparatus is the accurate measurement of residence or contact time between the coal and the steam. The actual contact time was measured by adding slugs of tagged coal to the feed stream and measuring the time interval as these slugs passed radiation detectors located outside the gasifier at each end of the isothermal zone. The tagged coal was prepared by adding a few milliliters of the extracted gallium solution to a few grams of coal and drying in a heated test tube. The gallium was extracted and dried on the coal within 5 minutes, producing about 1 millicurie of radiation (3.7×10^7 disintegrations per second).

Figure 1 illustrates this application. The tagged coal passes two scintillation crystal detectors connected through ratemeters to a recorder. Each time the tagged coal passes a detector, gamma radiation from the coal produces a peak on the tracing. The contact time is a function of the distance between these peaks. Reproducibility of measurement for contact times of 3 to 10 seconds is 2 percent.

Most of the gallium chloride remains in the ash residue collected at the bottom of the gasifier. With successive measurements, the gallium-68 contaminates the system, causing an increase in the background count and reducing the accuracy of measurement. When this happens, the system is shut down until the next day when all of the radioactivity will have completely disappeared.

This method has been used repeatedly to measure the residence time of a variety of coals with far greater accuracy than other methods of measurement. Moreover, the method gave qualitative information on the mixing of coal and steam and pinpointed the location of an unexpected holdup in the residue collector.

Adaptations of this method are being used in other applications. One of these is the measurement of the slippage of solids entrained in liquid and gaseous media moving at high velocities. Here, a high-speed recorder measures the speed of tagged material to thousandths of a second.

DISCUSSION

Germanium-68-gallium-68 is only one of many parent-daughter radioisotopes which can be used for a continuing supply of short half-life tracers. However, only a small number of these have practical significance from the standpoint of availability and appropriate decay characteristics. A cesium-137-barium-137 pair is commercially available as an automatic mechanical unit (2). The decay of tin-113 to indium-113m has been reported suitable for this use (3). Others include strontium-90-yttrium-90, tellurium-132-iodine-132, and molybdenum-99-technetium-99m (4).

The advantages of using gallium-68-germanium-68 for short half-life tracer applications are:

1. Application is completely safe and almost foolproof. Once the simple extraction of gallium from germanium has been made, the short-life gallium may be used in any process with complete assurance that no radioactivity will exist after a few hours. The main safety precaution is avoiding carry over of germanium in the gallium solution during extraction. We have found no trace of carry over using various techniques of extraction.

2. Only a small amount of radioactivity is needed even for repeated testing in the same unit. Since any contamination of equipment completely disappears in a few hours, there is no increase in background count after successive days and weeks of use.

3. There is no waste disposal problem beyond simply waiting a few hours.

4. The simple extraction of gallium from germanium can be completed in a few minutes and the short-lived product used to tag almost any solid or liquid material, either as a water or oil solution. A junior chemist, or chemical technician, should find this to be a simple procedure.

5. The short-life gallium is a strong gamma emitter; tagged materials can be detected through heavy-walled pipes or at distances of several feet.

6. A formal radioisotope laboratory is not required for this method, since the amount of radioactivity needed for most applications is very low; 1 to 2 millicuries of germanium is adequate for most applications. The extraction of gallium from germanium should be performed in a chemical hood. Beyond a portable survey meter and proper shielding or storage place for the separatory funnel of germanium, no special facilities are needed. As germanium-68 is a cyclotron-produced radioisotope, a license from the Atomic Energy Commission is not required. A potential user must only satisfy the supplier that he has the minimum instruments needed for safe usage. In our use of this method of tagging coal, the total personnel exposure was calculated to be less than 1 millirad per month; film badges and dosimeters did not show any exposure.

The disadvantages of this method largely depend on the application:

1. Large amounts of germanium-68 are not readily available. Cyclotron production is usually in millicurie quantities, so that the applications of gallium-68 are generally limited to laboratory and pilot-scale applications. For determining the flow rate in a heavy-walled pipeline, a millicurie of germanium is adequate but this method is not suitable for applications requiring large amounts of radioactive material.

2. Because of the short half-life of gallium-68, the actual measurement must be completed in less than an hour, or before the radioactivity drops too low to measure. This also limits the sample preparation time. However, the availability of 1 millicurie of gallium from 2 millicuries of germanium every half-hour permits wide experimentation in methods of sample preparation.

LITERATURE CITED

(1) Dotson, J. M., Holden, J. H., and Koehler, W. A., Ind. Eng. Chem. 49, 149 (1957).
(2) Mayer, W. L. and Anderson, R. L., Ind. Eng. Chem. 52, 993, (1960).
(3) Newacheck, R. L., Nucleonics 15, 122-5 (1957).
(4) Tucker, W. D., U. S. At. Energy Commission BNL-4908, (1960).

USE OF COAL TAGGED WITH RADIOACTIVE GALLIUM - 68 IN BUREAU OF MINES RESEARCH

FIGURE 1